Photosynthesis.

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PHOTOCHEMICAL reactions, more particularly those in which highly endothermic syntheses take place, have generally been considered as something apart from the ordinary chemical reactions of the laboratory, and, indeed, have at times savoured of the mysterious for the reason that they seemed to be impossible of realisation *in vitro*. Recent work, however, on the energy changes involved in chemical reaction has shown that there is no inherent mystery in photosynthesis, and that all reactions, including those of photochemistry and catalysis, are completely analogous and obey the same laws. Every complete reaction consists of three separate stages, with each of which is associated its characteristic energy change. In general, molecules in the free state exist in a phase which is non-reactive, and in order to carry out any reaction it is first of all necessary to bring them into a reactive phase. This, which is the first stage of the reaction, requires that a definite amount of energy should be supplied to each molecule, the amount necessary being the difference in energy contents of the initial phase and the particular phase necessary for the reaction in question. Each phase of a given molecule differs in energy content by a fixed quantity of energy characteristic of that molecule, which is called the molecular quantum of energy. It follows, therefore, that the amount of energy necessary to activate each molecule in the first stage of the reaction is exactly one or more molecular quanta.

The second stage of the reaction is the atomic rearrangement whereby new molecules are produced, and it is this stage, and this stage alone, which is represented by the equation of the reaction.

The third and final stage is the change in phase of the newly synthesised molecules, whereby they pass into their normal and non-reactive phases. These last two stages are both accompanied by an escape of energy, and in each of them the amount of energy lost per molecule is exactly one or more molecular quanta characteristic of the new molecules. If the sum of the amounts of energy evolved in the second and third stages is greater than that absorbed in the first stage, the reaction is exothermic; whilst an endothermic reaction is one in which the energy necessary for the first stage is greater than the total amount evolved in the second and third stages.

There are three methods by which the energy necessary for the first stage may be supplied. It may be supplied by a material catalyst, or as radiant energy in the form of heat or light. The action of a catalyst does not arise here, and need only be mentioned in order to guard against any misconception. Many reactions take place in solution without the apparent intervention of the first stage, but in such cases the molecules have been activated by the solvent which functions as a catalyst.

In general, it is a matter of little consequence whether a molecule is activated by heat or light—that is, by infra-red or ultra-violet rays—in view of the known integral relationships that exist between the frequencies at which a molecule can absorb energy. It is a matter of cardinal importance, however, in the case of highly endothermic reactions, in which the increment of energy required for the initial phase change is obviously a large number of molecular quanta. When a molecule absorbs energy at its principal frequency in the infra-red, it absorbs it in terms of its molecular quantum; but if it absorbs ultra-violet light the unit of energy absorbed is a quantum which is an integral multiple of the molecular quantum, the multiple depending on the phase in which the molecule exists. One single quantum of energy absorbed at the characteristic frequency in the ultra-violet is always sufficient to activate a single molecule for any reaction, however endothermic this may be.

An endothermic reaction, in the first stage of which each molecule requires a large number of molecular quanta to activate it, will obviously be very much easier to carry out by exposing the molecules to energy of their characteristic frequency in the ultra-violet, when the absorption of one quantum per molecule is sufficient, than by exposing them to infra-red radiation, when the reaction will not proceed until a specific number of quanta have been absorbed by each molecule. When, as is frequently the case, this specific number is ten or more, it is not surprising that the realisation of the reaction by means of heat becomes impossible from the practical point of view. Such a reaction, however, is readily brought about by the absorption of a single quantum by each molecule at its characteristic frequency in the ultra-violet.

This may be understood more clearly from a specific instance, namely, the decomposition of hydrogen chloride into hydrogen and chlorine. The molecular quantum of HCl is about $5 \cdot 7 \times 10^{-13}$ erg, whilst the quantum absorbed at the ultra-violet frequency is about $9 \cdot 7 \times 10^{-12}$ erg, which is seventeen times as large. The activation of an HCl molecule so that it may decompose requires seventeen molecular quanta, and this may readily be brought about by exposing the gas to radiant energy of the wave-length 203 $\mu\mu$, when the absorption of a single quantum per molecule is sufficient. In order to bring about this reaction by heat, it will be necessary for each molecule consecutively to absorb seventeen molecular quanta, without losing any by radiation during the process, before it can decompose. The preparation of hydrogen and chlorine from hydrogen chloride is therefore very difficult to carry out by the aid of heat, but is readily induced by light. Another highly endothermic reaction which may be realised photochemically is the synthesis of formaldehyde from carbon dioxide and water, for it has been shown that under the influence of light of wave-length 200 $\mu\mu$ the reaction takes place according to the equation $CO_2 + H_2O = CH_2O + O_2$. These two examples are sufficient to show that whilst there is no essential difference between any two chemical reactions, those that are highly endothermic can be realised in practice only by photochemical stimulation.

The photosynthesis of formaldehyde from carbonic acid is of great importance, because it undoubtedly forms the first step in the formation of the many complex substances produced in the living plant. Some recent work in Liverpool on this reaction has thrown light on the mechanism utilised by the living plant in carrying it out, and also on the general problem of the photosynthesis of vegetable products. Although the synthesis of formaldehyde has been carried out photochemically in the laboratory with light of wave-length 200 $\mu\mu$, this is certainly not the case in the plant, for there is present in sunlight no radiation of this wave-length. The plant must in some way carry out the reaction with the absorption of visible light, for it is well known that visible light only is necessary for the photo-assimilation of carbon dioxide. It has been shown experimentally that, if a visibly coloured basic substance be added to the aqueous solution of carbon dioxide, formaldehyde is produced on exposing the mixture to visible light. The coloured substance, being basic, forms a complex with the carbonic acid, and within such a complex the components possess an identical infra-red frequency; that is to say, the molecular quanta of the two are identical. The energy absorbed by the coloured component is radiated at this common infra-red frequency and re-absorbed by the carbonate component. The necessary increment of energy is thus gained by the carbonate component, which is converted into a molecule of formaldehyde and a molecule of oxygen. This type of reaction has been named photocatalysis, the coloured substance acting as photocatalyst. It has been proved that malachite-green, methyl-orange, and *p*-nitrosodimethylaniline act as photocatalysts in this reaction, and in the presence of carbon dioxide give formaldehyde on exposure to visible light.

It has been shown by Willstätter that chlorophyll as it occurs in the plant combines with carbonic acid, and hence there is little doubt that it functions as a photocatalyst. The green-coloured complex absorbs visible light, and the energy so absorbed is transferred to the carbonic acid through the identity of infra-red frequency, with the result that formaldehyde and oxygen are produced. Although this gives a satisfactory explanation of the mechanism by means of which the living plant is able to produce formaldehyde with the aid of visible light alone, the story is far from complete, for there are yet to be considered the formation of carbohydrates from the formaldehyde, and the details of the process whereby the oxygen set free in the photosynthesis is transpired by the plant as gaseous oxygen.

It was shown by Moore and Webster that aqueous solutions of formaldehyde on exposure to ultra-violet light are polymerised to reducing sugars, but no evidence was given of the nature of these sugars or of the wave-length of the light required. It has been shown more recently in Liverpool that the necessary wave-length of the light is $290\mu\mu$, which at once establishes the fact that the polymerisation is photochemically distinct from the synthesis of formaldehyde. It has also been shown indirectly that the polymerisation of formaldehyde can be photocatalysed; but this is of scientific interest only, since there is no need to postulate such a mechanism in the plant. On exposure to ultra-violet light the formaldehyde molecules are activated, and it is these activated molecules which undergo polymerisation to sugars, since it is well known that ordinary formaldehyde does not polymerise in this way. When the formaldehyde molecules are first produced by photosynthesis they are in the activated form, and may therefore lose energy in one of two ways, either by change of phase to produce ordinary formaldehyde or by polymerisation to give sugar molecules. But it has been proved that the photochemically activated molecules at once polymerise to sugar, and therefore the photochemically synthesised molecules do the same. There is thus no need to consider the activation of the formaldehyde in the plant, for it is already activated when produced. The absence, therefore, of free formaldehyde in the growing leaf is explained by the fact that the photosynthetic process from carbonic acid to sugar takes place without a break. (Baly, Heilbron, and Barker, *Trans. Chem. Soc.*, vol. 119, p. 1025, 1921.)

The mechanism of the process whereby the oxygen, which is produced with the formaldehyde in the photosynthesis, is transpired as gaseous oxygen is one of great importance in view of the energy changes involved. Willstätter has shown that chlorophyll is in reality a mixture of two substances, chlorophyll A and chlorophyll B, and that a molecule of chlorophyll B contains one atom of oxygen more and two atoms of hydrogen less than a molecule of chlorophyll A. Two atoms of oxygen, therefore, are required to convert a molecule of chlorophyll A into a molecule of chlorophyll B, and since this is the exact relation required in the photosynthetic operation it is impossible to believe that it is not utilised. It is in the highest degree probable that a molecule of chlorophyll A combines with a molecule of carbonic acid, and that this complex on exposure to light gives a molecule of activated formaldehyde and a molecule of chlorophyll B. Willstätter hesitates to accept this view, because he found that the ratio of chlorophyll B to A is not altered during photosynthesis; but since he also proved that the velocity of transpiration of the oxygen is equal to that of the absorption of carbon dioxide, this cannot be accepted as evidence. It means only that there is present in the leaf some mechanism whereby the chlorophyll B is deoxidised and reconverted into chlorophyll A. Willstätter has further proved that an aqueous solution of chlorophyll, saturated with carbon dioxide, decomposes on exposure to light, no measurable photo-assimilation of carbon dioxide taking place. This affords an additional proof that there is present in the living plant a mechanism for maintaining the chlorophyll equilibrium.

In the living photosynthetic cell there exist, along with the chlorophylls, two more pigments, carotin, $C_{40}H_{56}$, and xanthophyll, $C_{40}H_{56}O_2$, the relation between the two as regards oxygen being the same as that between chlorophyll A and B. It may therefore be suggested that carotin has the power of reducing chlorophyll B to chlorophyll A, itself being oxidised to xanthophyll. This is supported by Willstätter's observation that the ratio of xanthophyll to carotin is increased during the photosynthetic operation. This increase, though perfectly definite, is not large enough to decrease materially the amount of oxygen transpired.

The complete reaction, $H_2O + CO_2 = CH_2O + O_2$, is highly endothermic, and is accompanied by the absorption of about 150,000 calories per gram-molecule of formaldehyde produced; and it is interesting to note that one quantum of energy absorbed in the visible region by chlorophyll is not sufficient to induce the complete reaction, since 150,000 calories per gram-molecule is almost exactly one quantum per molecule at $\lambda = 200\mu\mu$. Certain quantitative experiments have shown that a possible explanation of this is to be found in the fact that the carbonic acid is partly activated by combination with the chlorophyll. Alternatively, it is possible that, whilst one quantum of energy at $\lambda = 200\mu\mu$ is required for the complete reaction with the escape of free oxygen, one quantum of visible light as absorbed by the chlorophyll is sufficient to induce the reaction

$$\text{Chlorophyll A} + H_2CO_3 = \text{chlorophyll B} + CH_2O.$$

It is scarcely necessary to point out that either of these alternatives amplifies the principle of photocatalysis as previously defined. In either case the completion of the reaction, whereby the oxygen is abstracted from the chlorophyll B and transpired into the atmosphere, must require a further supply of energy. This second amount of energy is doubtless absorbed by the carotin and xanthophyll, the absorption bands of which lie in the visible region and between those of chlorophyll, so that each can absorb visible light simultaneously and independently. This suggested explanation is now being investigated.

Reference may be made to some other work now in progress at Liverpool which has already given most promising and suggestive results. By the action of ultra-violet light on aqueous solutions of formaldehyde, several hundred grams of concentrated sugar syrup have been prepared. Analysis of this syrup has shown that the sole products of the polymerisation are hexoses, no trace of a triose or pentose having been found. This result is very striking in view of the greater possibility on the kinetic theory of the formation of sugars containing fewer than six carbon atoms. There can therefore be no possible doubt that the sole products of the polymerisation of the activated formaldehyde as photosynthetically produced in the living plant are also hexoses. Not only does this afford a ready explanation of the storage of starch in the chloroplast during the period of photosynthetic activity and its subsequent hydrolysis to hexoses, which are utilised by the plant in later syntheses, but it also establishes the fact that pentoses must be formed from hexoses, possibly through furane compounds; further, it opens the door to most promising theories of the synthesis of other plant products, every stage of which is attractive in its simplicity.

Then, again, there is the question of the production of the various nitrogen compounds in the plant, which is one of considerable interest, since it would seem that the principal source from which the plant derives its nitrogen is potassium nitrate. It is well known that metallic nitrates are readily converted to nitrites by material catalysts as well as by ultra-violet light. Baudisch has shown that an aqueous solution of potassium nitrite and methyl alcohol, on exposure to ultra-violet light, gives formhydroxamic acid, the alcohol first being converted to formaldehyde. This has been confirmed at Liverpool by investigation of the action of ultra-violet light on aqueous solutions of potassium nitrate or nitrite containing formaldehyde, and it has been proved that an activated molecule of formaldehyde combines with a molecule of potassium nitrite according to the equation $CH_2O + KNO_2 = CH(OH){:}NOK + O$, since the reaction takes place only in the light. It has also been found that if the activated formaldehyde is in excess formhydroxamic acid and hexoses are simultaneously and independently produced. This condition is doubtless that which obtains in the plant, and it may be concluded that the two syntheses take place in the leaf without mutual influence. It is worthy of note that the photosynthesis of formaldehyde and the synthesis of formhydroxamic acid are both accompanied by the setting free of oxygen.

Experiments are also in progress on the reaction between activated formaldehyde and ammonia, and although these are not yet complete, they have already established the great reactivity of activated formaldehyde towards ammonia. Whatever, therefore, may be the starting point on the nitrogen side, potassium nitrate or ammonia, there is no question that, in the presence of activated formaldehyde such as is produced photosynthetically in the plant, compounds are formed in which carbon and nitrogen are united, thus securing the first step towards protein, pyrrole, and alkaloid synthesis.

Finally, one very important deduction may be made. The sole photosynthetic process in the living plant would seem to be the production of activated formaldehyde from carbon dioxide and water. These activated molecules either polymerise to hexoses or react with potassium nitrite or ammonia. Any further reactions are not photochemical except in so far that the first synthesised nitrogen compounds combine with more molecules of activated formaldehyde to give complex nitrogen derivatives.

The Migration of British Swallows.

By Dr. A. LANDSBOROUGH THOMSON, O.B.E.

> "Sister, my sister, O fleet sweet swallow,
> Thy way is long to the sun and the south."
> SWINBURNE.

FROM time immemorial the Swallow (*Hirundo rustica*, Linn.) has been a proverbial type of summer visitor to our northern lands, but age-long familiarity with the fact of its seasonal appearance and disappearance has not served to bring us complete knowledge or understanding: there are many secrets, both matters of fact and questions of interpretation, to which we have as yet no clue. Nevertheless we are in a better position to appreciate the problem than were Gilbert White and his contemporaries, who were obsessed with the idea that hibernation, particularly in regard to this species, might play an important part as an alternative to migration. White was particularly influenced by the frequent phenomenon of the few "early swallows" which appear some time before the main contingents arrive, and are no more seen if wintry weather should recur in the meantime. The theory of hibernation dies hard even to-day, and every now and then some imperfect piece of evidence in its